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Characterization and evaluation of the hydraulic activity of water-cooled slag and air-cooled slag

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Abstract

Water-cooled slag (WS) and air-cooled slag (AS) were characterized chemically and mineralogically and a comparative study of their reactivities with 10% and 20% lime was conducted using an accelerated chemical method. Both types of slag have the same chemical composition, but WS is completely vitreous materials and the main mineral composition of AS is gehlenite. The kinetics of the WS–lime and AS–lime reactions were investigated in suspension by the determination of the proportions of unreacted lime and the combined water up to 28 days. Both slags underwent hydration at room temperature. The rates of hydration were rapid in the first 3 days, but subsequently it depressed due to the formation of dense layer of hydration products on the unhydrated slag grains. The hydration products were identified by X-ray diffraction (XRD) and SEM combined with EDX. The hydration products formed depend on the lime contents. The results obtained suggest that AS may be used in the production of low strength building units or may be used with WS in the production of slag cement.

Keywords: Hydraulic activity; Air-cooled slag; Water-cooled slag; Gehlenite; Hydrogarnet

1. Introduction

Although water-quenched blast furnace slag (BFS) has been used to produce slag cement for a long time, other slags such as air-cooled BFS and steel making slag are not used. The feasibility of using these types of slags has been disregarded due to the prejudgment that air-cooled slags (AS) are hydraulically unreactive. Consequently, use of these slags is minimal or they are only used in low value applications [1]. However, it has been reported [2,3] that the cooling conditions are not the only factor determining the hydraulic activity. Demoulian et al. [4] found the presence of up to 5% of crystalline phases increased the hydraulic activity and up to 30% had no detrimental effect on the compressive strength of blended cement concrete.

As a rule, the phase composition, the structure and the hydraulic activity of a slag all depend on its chemical composition and thermal history. At the same time, the chemical composition exerts a complicated influence on the slag structure and governs the effect of cooling conditions on the glass contents. Daugherty et al. [5] and Yuan et al. [6] found the glass fraction became easier to produce as the acidity of the slag increased for a series of slag compositions prepared from reagent grade chemicals. It was also found that air-cooled BFS with a modulus of basicity $M_b = 1[M_b = (CaO + MgO)/(SiO_2 + Al_2O_3)]$ contained approximately 50–70% by mass of crystalline phases. Highly basic slags with $M_b = 1.5$ are mainly crystalline. A glassy structure is formed in acidic slags that contain essential amounts of aluminum even with slow cooling [3]. These results appear to have stimulated a reconsideration of the hydraulic properties of steel-making slag and air-cooled BFS [7–11].

Sharma et al. [10] found that air-cooled blast furnace and phosphorous furnace slags were not suitable for the manufacture of slag cements, but that these slags could

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Table 1
Chemical composition of AS and WS

	SiO_2	CaO	Al_2O_3	Fe_2O_3	BaO	MgO	MnO	TiO_2	Na_2O	K_2O	SO_3	S^{2-}	LOI	Total
WS	34.2	36.5	10.5	0.44	5.31	2.45	6.24	0.72	1.84	0.71	0.01	0.95	− 0.98	99.2
AS	35.3	36.2	10.8	1.87	6.63	1.35	4.48	0.46	1.47	0.43	0.01	0.75	− 0.80	99.7

Negative values due to the oxidation of sulfide and ferrous iron.

be used after thermal activation or chemical activation. The test results of Hwang and Lin [11] indicate that the strength development of AS was better than expected, even though it was lower than that of water-quenched slags. However, even if these slags cannot fulfill the requirements of the standard specifications for slag in blended cements, their hydraulic activity can be exploited in many other building materials. These may include autoclaved building materials or bricks. The latter may be an economical alternative for developing countries because the technological development required is very small.

Our aim is to chemically and mineralogically characterize two slags produced from the same blast furnace, but which differ in their rates of cooling. This is the primary step in a project to investigate the utilization of these and other by-products in building materials. The hydraulic activities of the slags were studied using an accelerated chemical method, in which the slag–lime reaction in suspension was followed with time. Under these conditions the amounts of lime combined with latent hydraulic materials reach appreciable values within relatively short times and the reaction products, in particular the hydrated phases containing Al_2O_3, are sufficiently well crystallized to be identified without difficulty by X-ray diffraction (XRD) [12]. This technique is very convenient in permitting the simultaneous analysis of the solid and liquid phases. Such characterization enables a better understanding of the hydration phenomena and a comparison of the hydration kinetics between different slags could be established.

2. Materials and methods

The AS and water-cooled slag (WS) used throughout this investigation were obtained from Halwan Steel in Egypt. These slags were obtained from the same blast furnace and the same raw materials. AS is produced by slow cooling in air due to inadequate granulation facilities. Both slags were ground in a ball mill to obtain a Blaine surface area of 300 m^2/kg. WS and AS were characterized by chemical analysis, XRD, FTIR, SEM and optical microscopy.

To study the hydraulic activity, the materials were mixed with 10 and 20 wt.% lime [$Ca(OH)_2$]. In a typical experiment 5 g of a mix was added to 75 ml of decarbonated distilled water in a polyethylene bottle (W/S = 15). The slurries were hydrated for 0.5, 1, 3, 7 and 28 days with occasional shaking using a mechanical shaker. The progress of the reactions was followed by analyzing the solid phases after separation by filtration through a sintered glass filter. The hydration reaction was stopped by immersing the solid phase in about 100 ml of a (1:1) methanol/acetone mixture and magnetically stirring for 30 min. The solid was filtered off, washed with methanol then dried at 105°C for 24 h. The dried samples were tested for free calcium hydroxide using the modified Franke method [13]. The combined water contents were calculated from the loss on ignition at 900°C after correction for the loss in weight due to free calcium hydroxide and the gain in weight due to the presence of ferrous iron and sulfide. The phases present were determined by XRD. XRD analyses were performed using an automated diffractometer (Scintag, Sunnyvale, CA) at a step size of 0.02°, scan rate of 2°/min, and a scan range from 4° to 60° 2θ. A single beam infrared spectrometer (FT-IR) (MB100, Bornem/Hartmann & Braun, Quebec City, Canada) was used, and spectra were obtained over the wave number range of 400–4000 cm^{-1} at a resolution of 3 cm^{-1}. The KBr (Spectroscopic grade, Aldrich Chemical, Milwaukee, WI) drifts technique was used with a KBr/sample ratio of 100/1.

3. Characterization of the raw materials

The chemical analyses of WS and AS are given in Table 1. WS and AS have nearly identical chemical compositions. Table 2 compares the mean chemical compositions of these

Table 2
Comparison of the composition of the Egyptian slags studied and slags described in the literature

	Present slags	Demoulian et al. [4]		Moir and Glasser [14]	
	Mean	Min	Mix	Min	Mix
SiO_2	34.8	32.0	37.3		
CaO	36.4[a]	37.9	44.4		
Al_2O_3	10.7	10.3	16.0		
Fe_2O_3	1.20	0.30	9.30 (FeO)		
BaO	6.0[a]	low			
MgO	1.9[a]	3.60	8.70	3.3	11.7
MnO	5.4[a]	0.34	1.31	0.25	1.2 (Mn_2O_3)
TiO_2	0.6	0.49	0.65	0.22	1.7
Na_2O	1.66[a]	0.25	0.50	0.17	0.9
K_2O	0.57	0.44	0.98	0.29	0.96
Cl	0.01	0.003	0.31	0.001	0.22
SO_3	0.01	0.00	0.19		
S^{2-}	0.85	0.48	1.26	0.5	2.8

[a] Outside the range of published values for blast furnace slags.

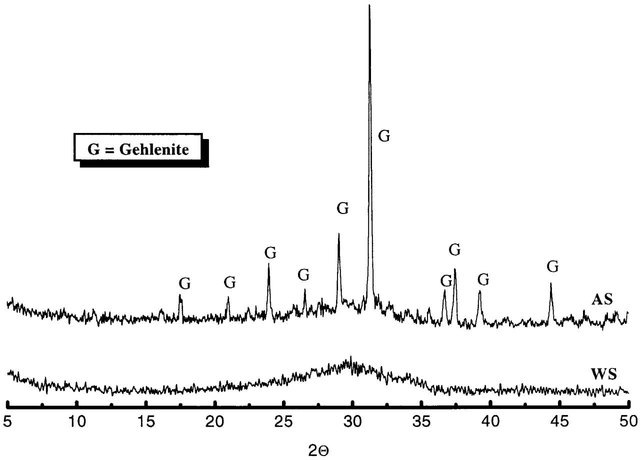

Fig. 1. XRD of WS and AS.

slags with those of slags described in the literature. The slags of present interest differ in chemical composition from typical BFS. The Egyptian slags studied are high in BaO (6.0%), MnO (5.4%) and Na_2O (1.66%), but low in MgO (1.9%). The X-ray diffractograms of WS show it to be completely vitreous and with an amorphous hump characteristic of the glass at 28° 2θ (Fig. 1). This corresponds to a *d* value of 30.70° A consistent with the amorphous phase being constituted of network-forming oxides SiO_2 and Al_2O_3 [15].

The mineralogical composition of AS as identified from XRD reveal the main mineral in AS to be gehlenite ($Ca_2Al_2SiO_7$) [JCPDS# 35-0755] (Fig. 1). A considerable proportion of amorphous material as indicated from the hump, which coincides with the hump of WS, is also present. The short-range (interatomic) order was explored by FTIR. Fig. 2 shows the FTIR spectra of WS and AS. Generally, the strongest absorbance bands occur at 1094, 800 and 470 cm^{-1}, characteristic of the four coordinated silica [16]. Broadening and, the first two of them that are attributed to asymmetric and symmetric stretching of Si–O–Si, are shifted to lower frequency. The low-frequency shift in these bands arises from the increasing contribution made by Si–O–Al linkages at the expense of Si–O–Si linkages [16–18]. The spectrum of AS shows a group of broad bands in the range 800 to 1100 cm^{-1} which are characteristic of gehlenite [19]. The FTIR spectra of WS is similar to that of AS in that the positions of the band envelopes remain much the same. However, the bands are broadened and fine structure is lost. This is consistent with the resemblance of the IR spectra of a glass and a crystalline solid with a similar composition [16]. The microstructural differences between WS and AS could not be readily distinguished by SEM. Optical transmitted microscopy indicated that AS contained glass and that WS contained a very small amount of crystalline material. However, the latter could not be detected by XRD.

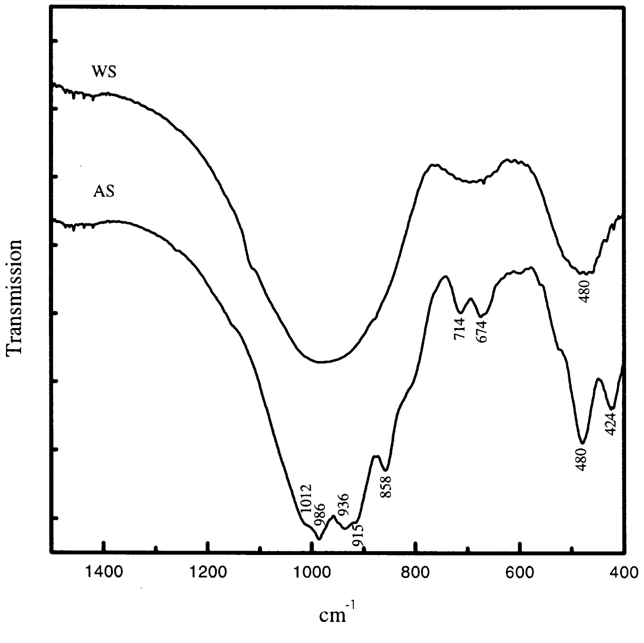

Fig. 2. FTIR spectra of AS and WS.

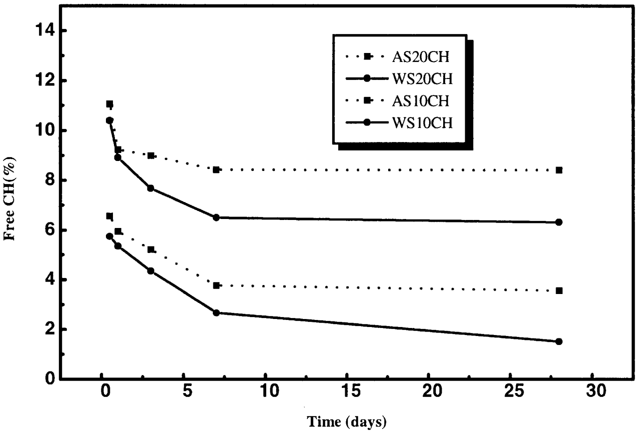

Fig. 3. Free lime contents at different times.

The chemical analysis data indicate that both slags fulfill the chemical requirements of the ASTM and the

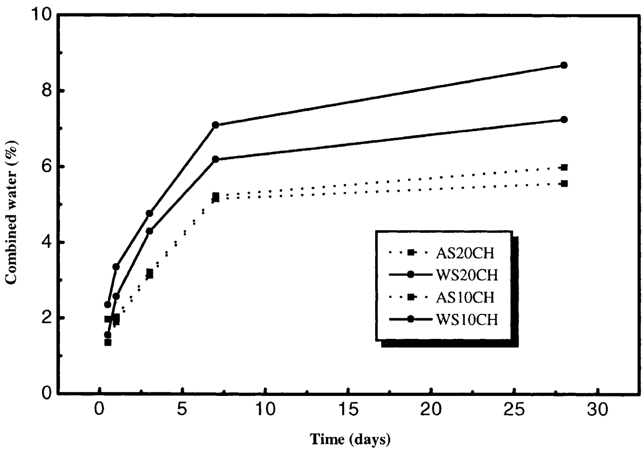

Fig. 4. Combined water contents at different times.

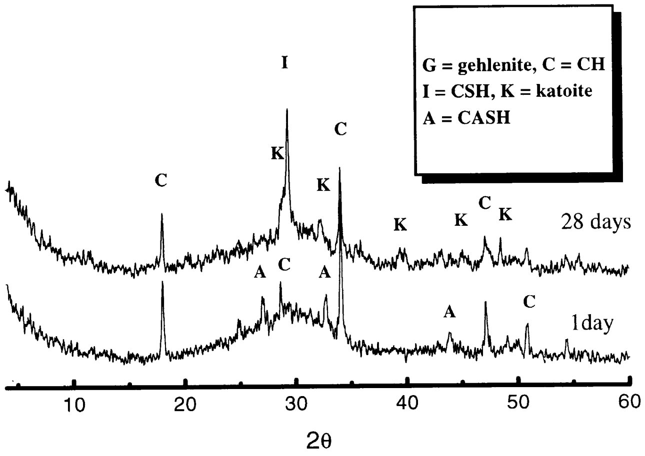

Fig. 5. XRD of WS + 20% CH hydrated in suspension.

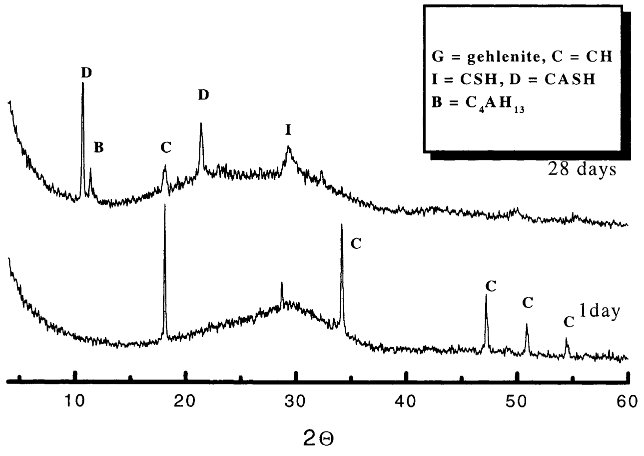

Fig. 7. XRD of WS + 10% CH hydrated in suspension.

British Standard for a slag to be used in blended cements. The basicity of WS is 1.45 and that of AS is 1.37, using $(CaO + MgO + 1/3Al_2O_3)/(SiO_2)$. However, AS does not fulfill the glass content requirement of either standard.

4. Reaction kinetics in suspension

Kinetics of hydration were assessed by determining the chemically combined water contents (Wn) and free calcium hydroxide contents at different times of hydration. The results of free calcium hydroxide determination are shown in Fig. 3, and the variations in combined water are shown in Fig. 4. The free calcium hydroxide contents decrease sharply during the first day of hydration. A continuous decrease in free calcium hydroxide occurred at a slow rate during the next 6 days. During this period the consumption of calcium hydroxide is associated with the increase in the combined water contents. The difference between AS and WS mixes in free calcium hydroxide and combined water contents reflect the difference in their hydraulic reactivity. In the period from 7 to 28 days there are minimal changes in the free calcium hydroxide and combined water contents.

XRD analyses of the phases present in the high lime mixes (AS20CH and WS20CH) after 1 and 28 days (Figs. 5 and 6) reveal the main hydration products to be calcium silicate hydrate gel and the hydrogarnet phases. WS and AS mixes hydrated for 1 day show the presence of calcium aluminum silicate hydroxide $(Ca_3Al_2(SiO_4)(OH)_8)$ [JCPDS# 32-0151], which is a member of the hydrogarnet solid series $(C_3AH_6-C_3AS_3)$. After hydration for 28 days, the WS mix (Fig. 5) shows that calcium aluminum silicate hydroxide has transformed to katoite [JCPDS# 77-1713] (with nearly the composition $Ca_3Al_2(SiO_4)_{0.64}(OH)_9$), which is also another member of the hydrogarnet series. The peak characteristic of the CSH gel has also intensified. After 28 days of hydration, the AS mix also contains katoite

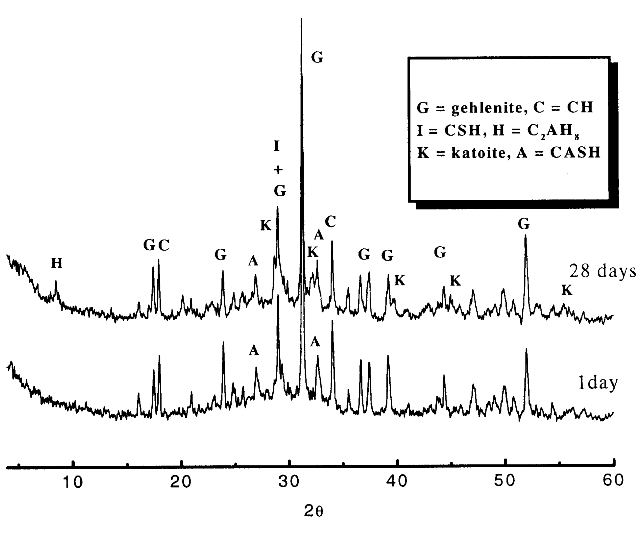

Fig. 6. XRD of AS + 20% CH hydrated in suspension.

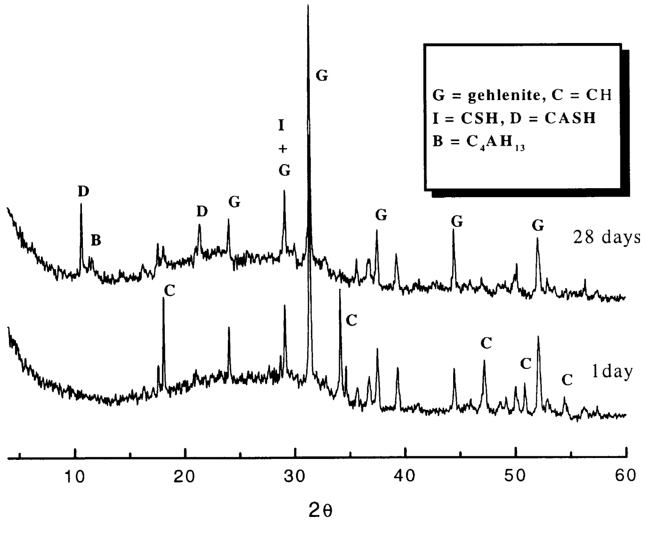

Fig. 8. XRD of AS + 10% CH hydrated in suspension.

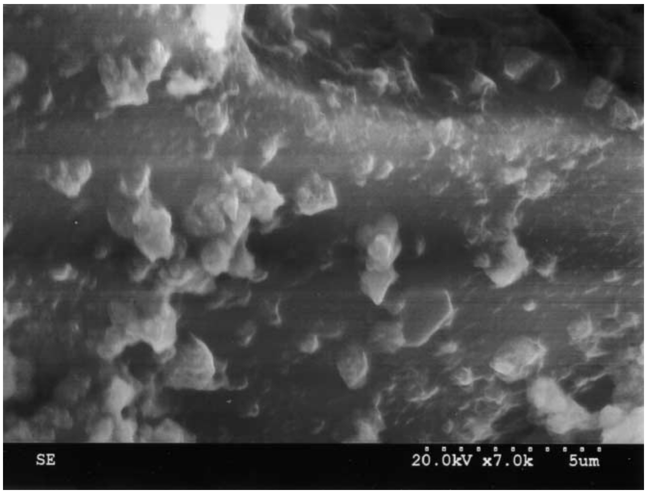

Fig. 9. SEM of mix AS20CH hydrated for 1 day.

with $Ca_3Al_2(SiO_4)(OH)_8$ and the AFm phase (C_2AH_8) [JCPDS# 11-0205] is formed.

XRD analyses of the phases present in the low lime mixes (AS10CH and WS10CH) after 1 and 28 days (Figs. 7 and 8) reveal also the main hydration products to be calcium silicate hydrate gel and the calcium aluminum silicate hydrate; $CaAl_2Si_7O_{18}\cdot1.7H_2O$ [JCPDS# 21-0132]. Calcium aluminum oxide hydroxide hydrate ($Ca_2Al(OH)_7\cdot3H_2O$) [JCPDS# 33-0255] is also present in both low lime slag mixes.

Fig. 9 shows the SEM micrograph of mix AS20CH hydrated for 1 day. The micrograph indicates that the hydration products formed as patches upon the surface of slag grain, thus allowing further lime to react with the slag. However, as hydration proceeds the hydration products overgrow the slag grains, forming a dense layer, as shown in Figs. 10 and 11, which show the micrographs of mix AS20CH and mix WS20CH, respectively, hydrated for 28 days. These results are consistent with the diminishing rates of free calcium hydroxide and nonevaporabale water uptake.

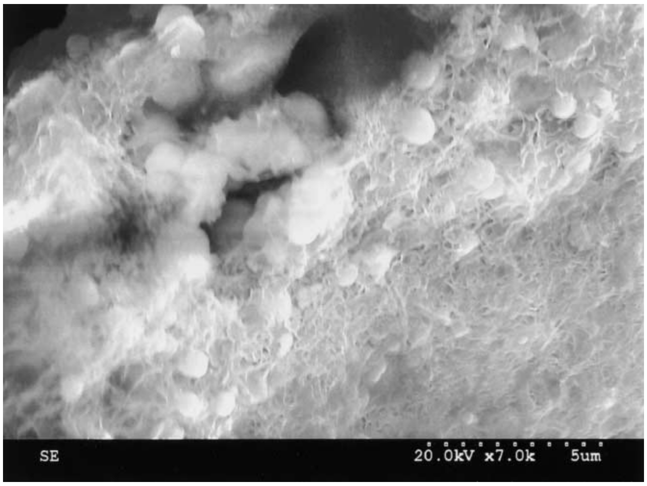

Fig. 10. SEM of mix AS20CH hydrated for 28 days.

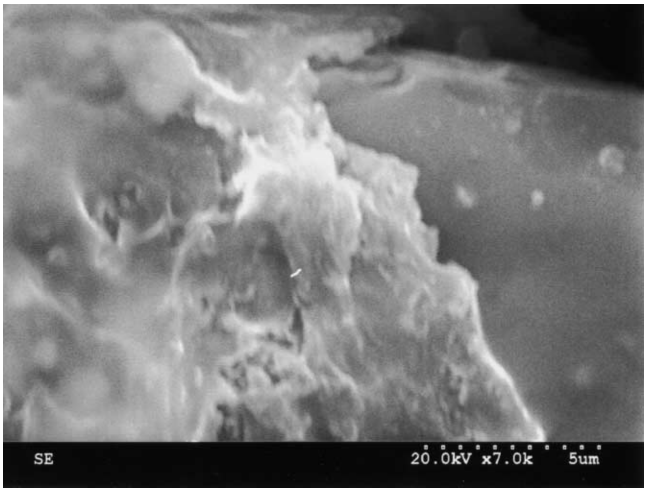

Fig. 11. SEM of mix WS20CH hydrated for 28 days.

5. Conclusions

Both the AS and WS slags studied are hydraulically active. As expected, WS shows higher activity than AS. The hydration products of slag–lime mixes in suspension depend on the lime contents. In high lime mixes (20% CH) calcium silicate hydrates and various hydrogarnet series compositions formed. Calcium aluminum silicate hydroxide ($Ca_3Al_2(SiO_4)(OH)_8$) is formed in both types of slag after hydration for 1 day. This transforms to katoite [$Ca_3Al_2(SiO_4)_{0.64}(OH)_9$] by 28 days in the WS20CH mix. It partially transformed to katoite in the AS20CH mix and was accompanied by the formation of AFm phase (C_2AH_8).

Calcium silicate hydrate, calcium aluminum silicate hydrate ($CaAl_2Si_7O_{18}\cdot1.7H_2O$) and calcium aluminum oxide hydroxide hydrate ($Ca_2Al(OH)_7\cdot3H_2O$) are also formed in both low lime (10% CH) slag mixes during 28 days of hydration. This suggests that hydrogarnet phases are only stable at high lime contents. The present study is in agreement with the results of de Silva and Glasser [20] who studied the phase equilibrium in metakaolin–lime mixes. They found that silicon-containing hydrogarnets are relatively stable in CH-rich mixes in the temperature range up to 55°C. In the lime-poor part they found CASH gel tends to form, which act as precursors for zeolite formation. Low-lime mixes in the present investigation tends to form calcium aluminum silicate hydrate ($CaAl_2Si_7O_{18}\cdot1.7H_2O$) at 28 days hydration, but no Al-containing crystalline phases were detected at 1 day hydration, which may indicate the formation of CASH gel as the initial hydration products in these mixes.

Although AS is less reactive than WS, the pozzolanic activity tests show it be hydraulically active. Therefore, AS may be useful in the production of low slag cement or other building products produced at elevated temperatures.

Acknowledgments

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